Achieving Interligand Charge Transfer in Imidazolium-based Carbene-M-Amides (CMAs)

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Abstract

iPr is an **imidazolium-based carbene** with a high energy lowest unoccupied molecular orbital (LUMO). The high LUMO makes iPr a **weak e⁻ acceptor**. Thus, in the study of Carbene-Metal-Amides (CMAs), iPr is underutilized because iPr-bearing CMAs do not achieve **interligand charge transfer (ICT**) with conventional amide donors such as carbazole. The weak e⁻ accepting ability of iPr can be overcome by using strong e⁻ donating amides.

This work highlights three new Au-containing CMAs bearing imidazolium-based carbenes (acceptors) and **electron-rich amides**. Their room-temperature photophysical properties were characterized in toluene, THF, and polystyrene (PS) films. This work highlights how carbene acceptor strength can change solvatochromism. All new CMAs display visible emission with peak maxima from 459–501 nm in fluid solutions and 460–472 nm in PS. CMA3 achieves 100% photoluminescence quantum yield in fluid solutions.

Introduction

Carbene-Metal-Amides (CMAs) are a class of coinage metal (M=Cu, Ag, Au) compounds. When excited by light, the carbene acts as an e⁻ acceptor while the amide acts as an e⁻ donor, enabling an **interligand charge transfer (ICT) excited state (ES)**[1].

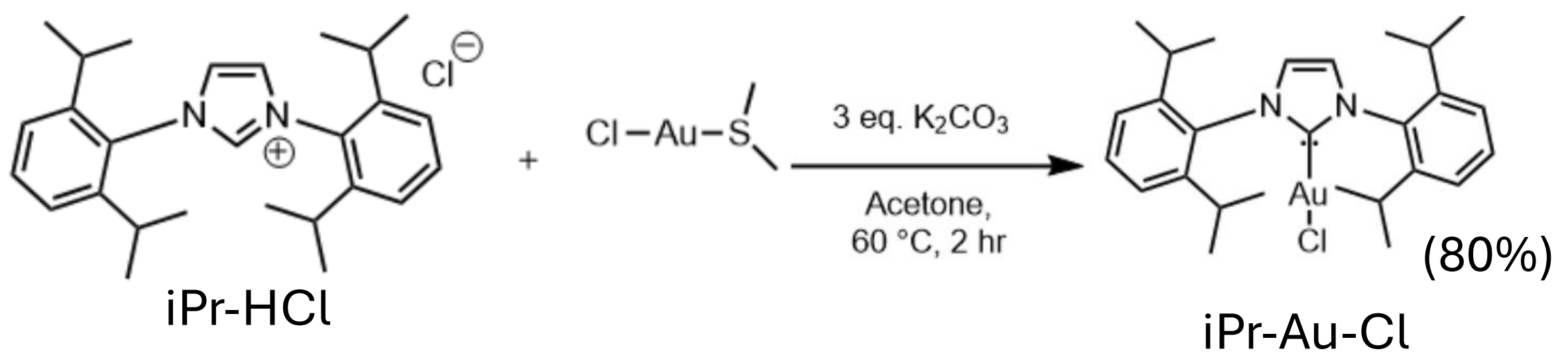
Photophysical characteristics can be tuned by changing the donor or acceptor ligands. This tunability gives CMAs potential for diverse applications such as dopants in organic light-emitting diodes (OLEDs)[1] or photosensitizers in photoelectrocatalysis[2].

ICT was achieved by pairing the imidazolium carbenes with **electron-rich amides**, which are strong e⁻ donors. Room-temperature photophysics were characterized to elucidate the effects of **carbene acceptor strength** and **amide rigidity.**

Measurements were made in toluene, THF, and PS films to see the effect of nonpolar fluid, polar fluid, and rigid media.

Methods

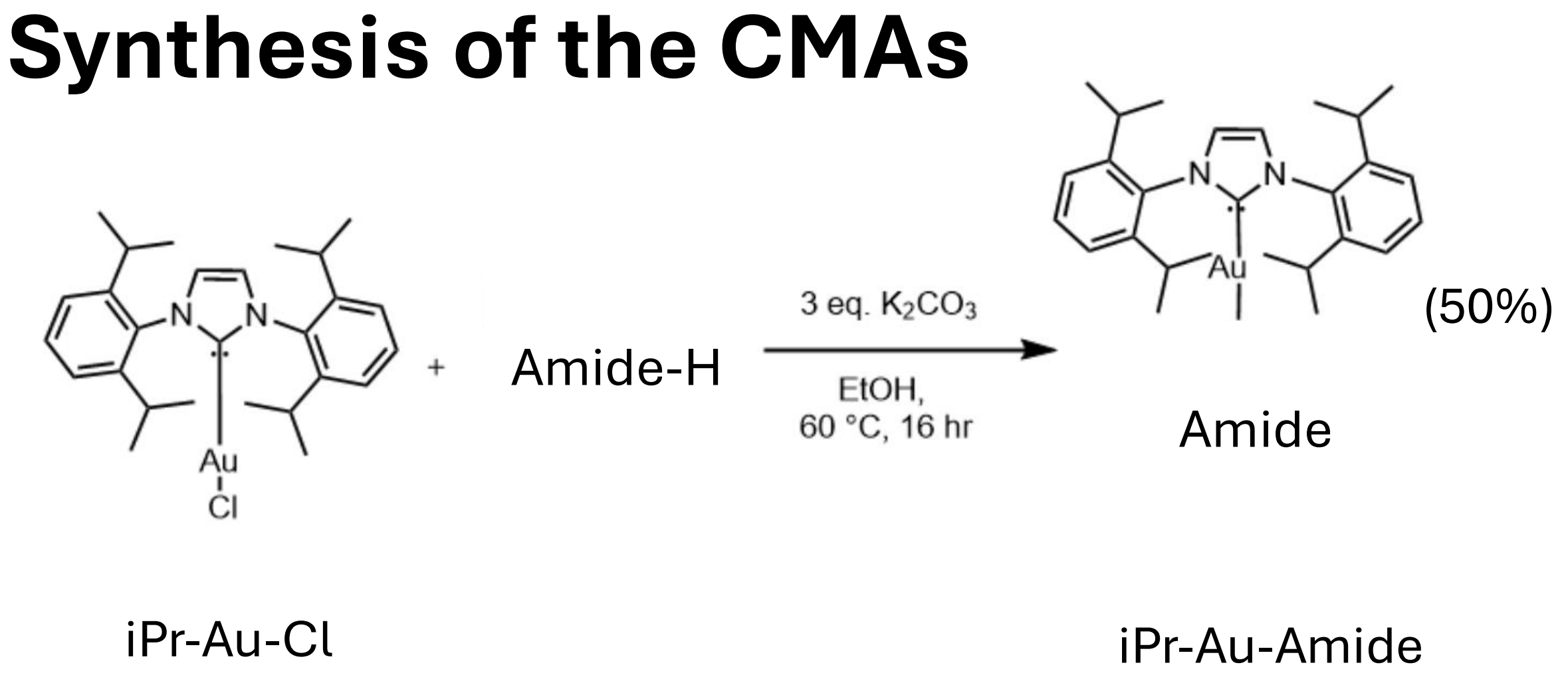
Synthesis of iPr-Au-Cl and SiPr-Au-Cl



Workup Procedure

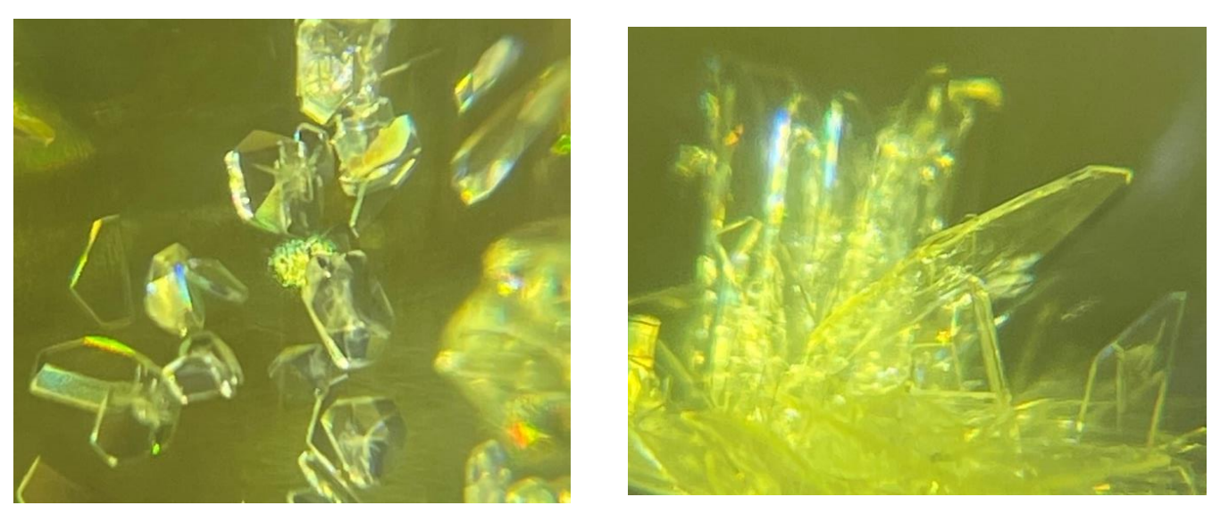
1) Rotovap the mixture to dryness
2) Dissolve the product in DCM, filter off the base through celite
3) Concentrate the solution, add pentanes, allow the product to precipitate in a -40 °C freezer over 30 min
4) Filter off the solid product

Synthesis of the CMAs



1) This workup procedure is the same as above, except it uses THF instead of DCM.
2) The same methods were used to synthesize all CMAs.

Crystallization



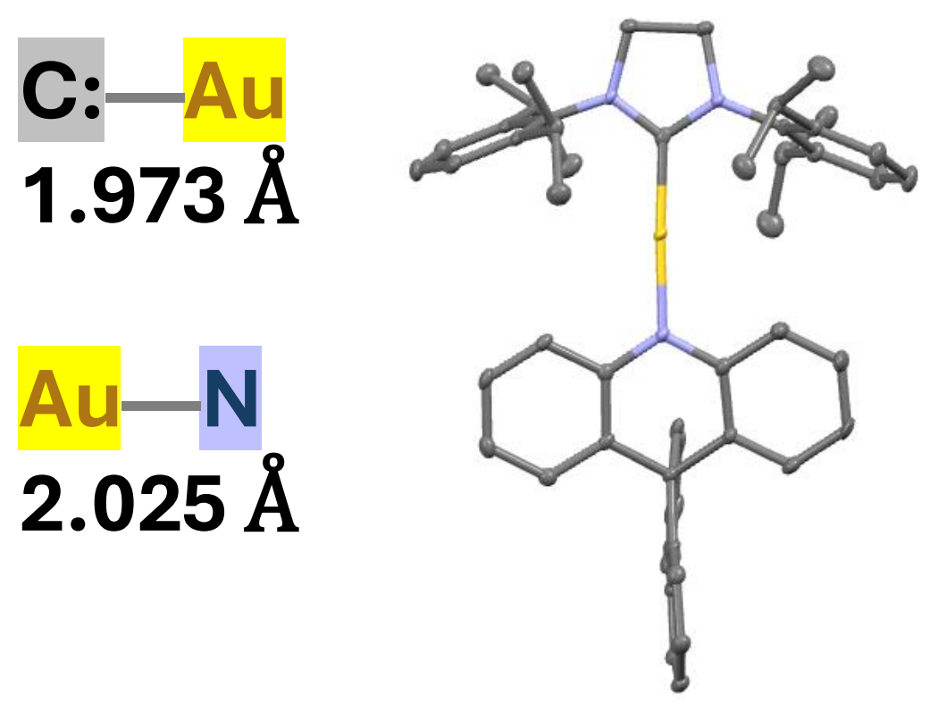
X-Ray quality crystals

Vapor diffusion was used for bulk purification and to grow single crystals suitable for x-ray diffraction. Antisolvent diffuses and slowly layers onto the CMA solution so that the CMA molecules can organize into an ordered structure, producing crystals.

1) Made saturated THF solution of the CMA. Filter directly into vials
2) Sealed the vials with Teflon tape, then punctured with several holes
3) Place the vials in jar containing a shallow bath of antisolvent (pentanes)
4) Place on a pad and do not disturb for at 1-4 days; carefully decant the liquor and harvest crystals

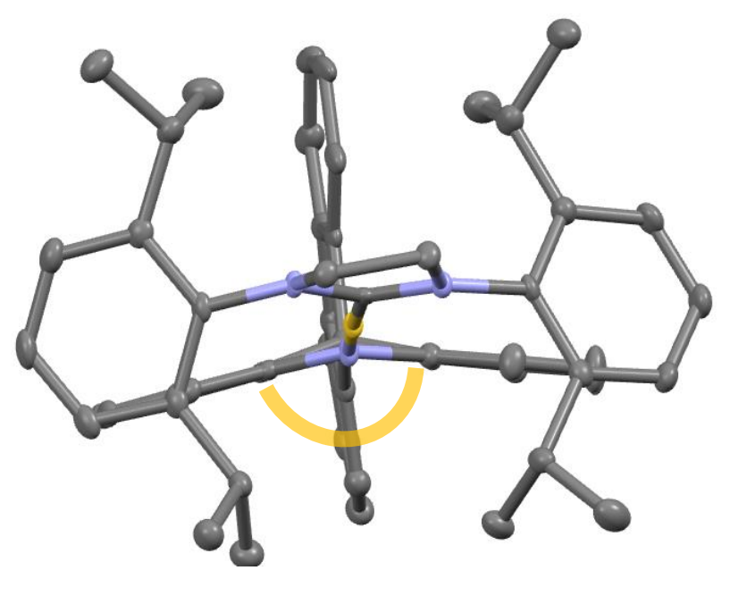
Results & Discussion

X-Ray Crystal Structure



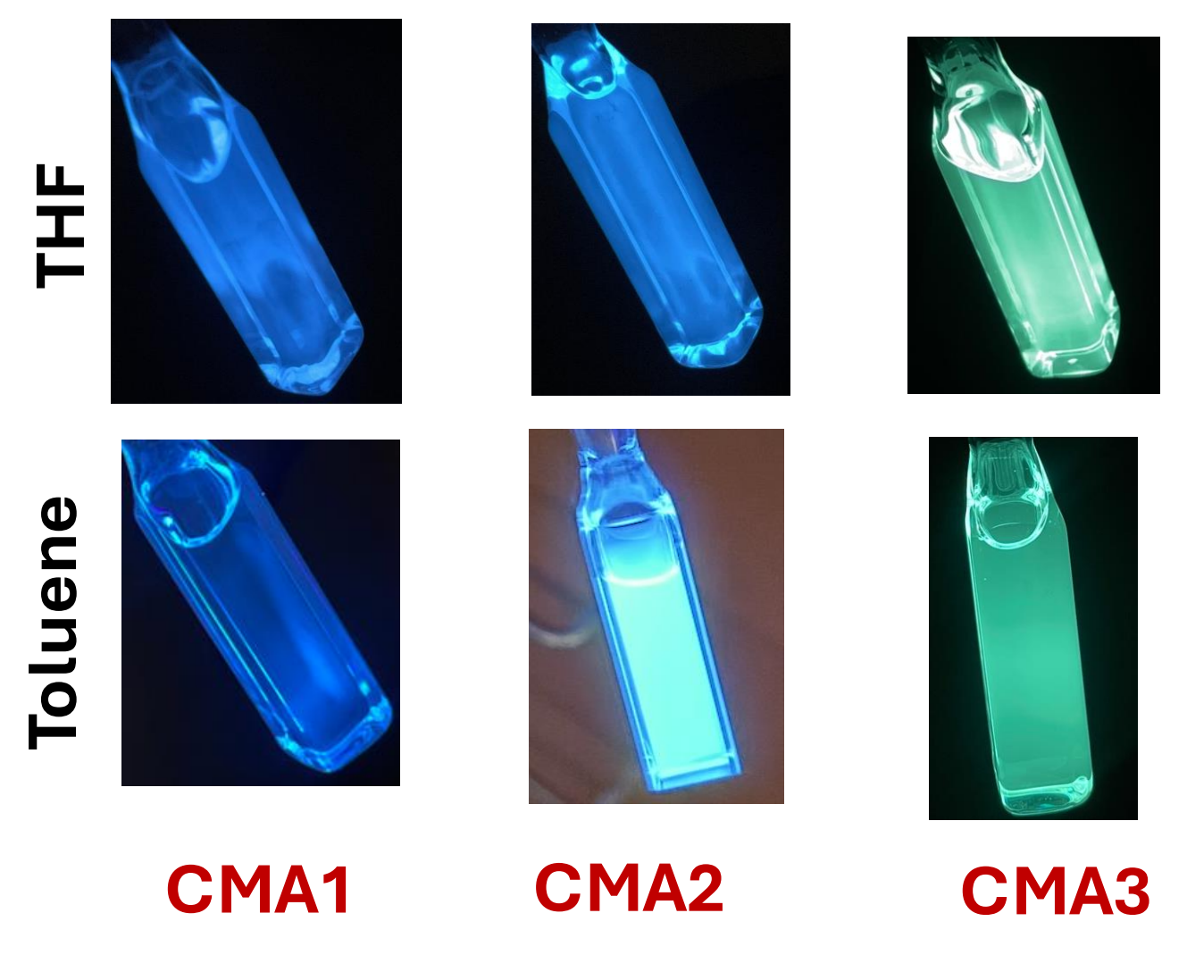
(Left) X-ray crystallography reveals that CMA3 is nearly linear (**$\angle_{\text{C-Au-N}}$ = 177°). The** C:–Au–N bond distances fall within a typical range for Au CMAs.

(Right) The acridine moiety is bent. The central ring is slightly puckered, but the outer rings remain planar. The planes of the outer rings intersect to make a 160.8 ° angle.

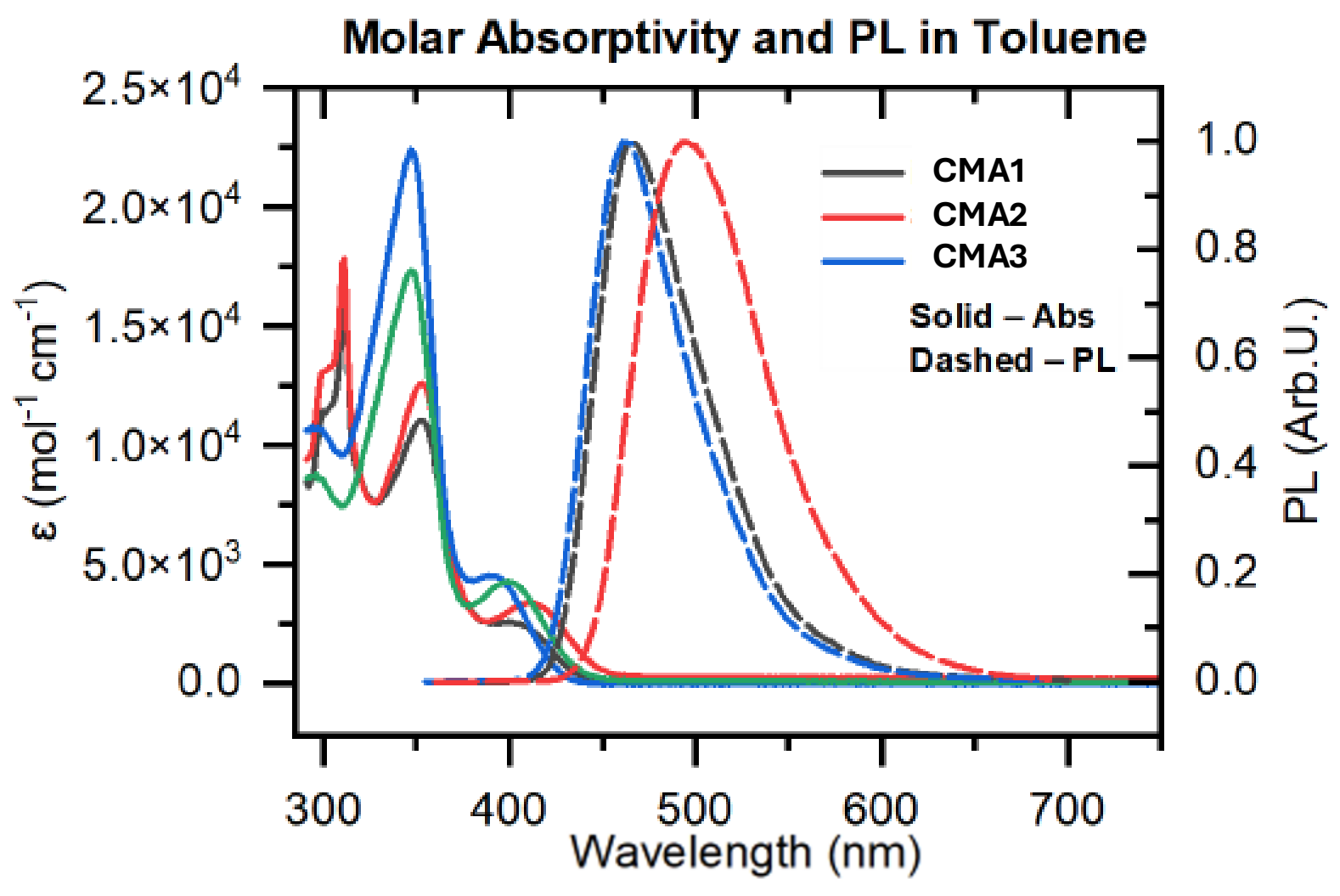


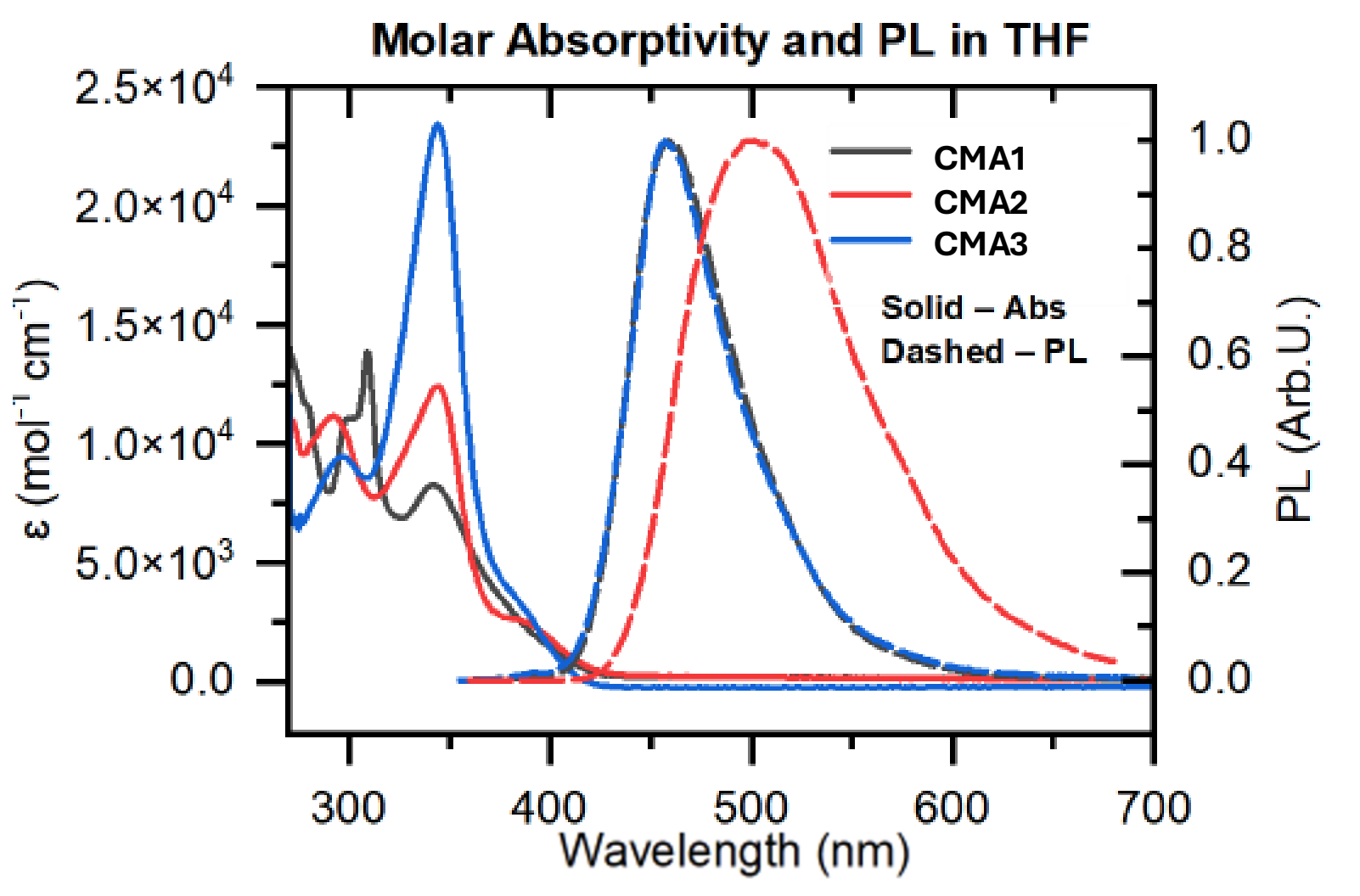
160.8°
View looking down the C:–Au–N axis with the iPr ligand in front.

Fluid Solution Photophysics

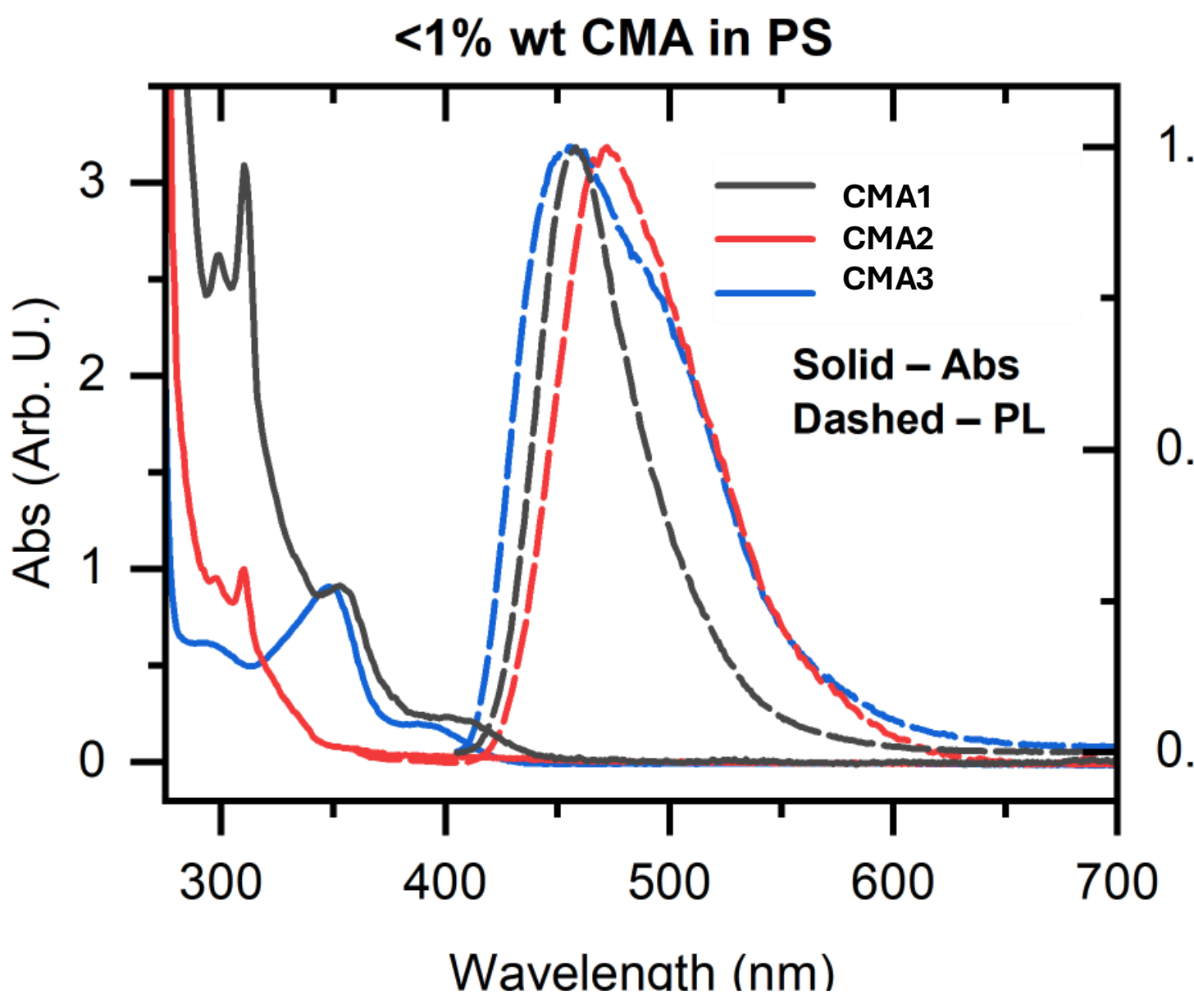


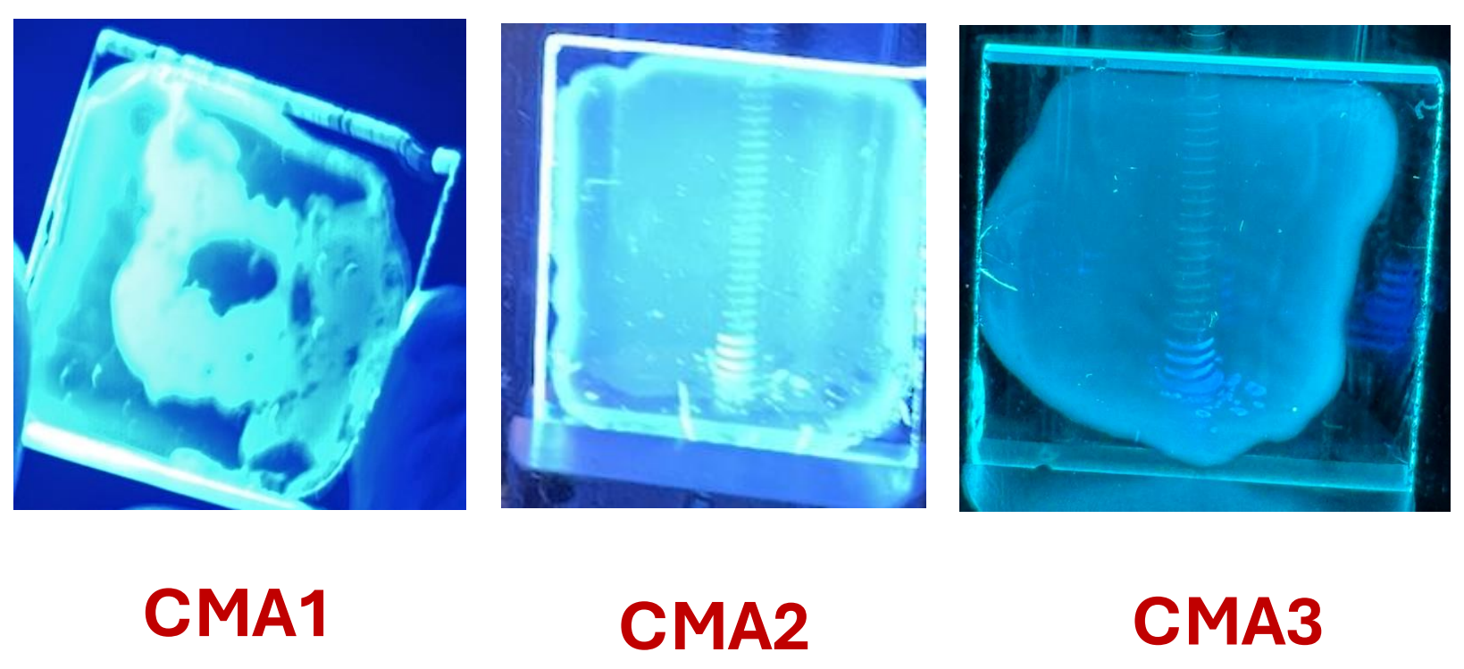
N₂ (g) sparged solutions





Polystyrene Film Photophysics





Takeaways

1) ICT character is dependent on the acceptor strength of the carbene.
2) CMA3: $\Phi = 1$ in both toluene and THF. It has the shortest fluid solution lifetime of τ = 190 ns in toluene.
3) Φ improved in PS compared to fluid solution, except for CMA3: PS film must be remade to repeat experiment.

Acknowledgements

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X-ray diffraction was performed and crystal structure was solved by Ao Jiao.

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